



Article

# [2+2] Cyclo-addition Reactions for Efficient Polymerisation on a HOPG Surface at Ambient Conditions

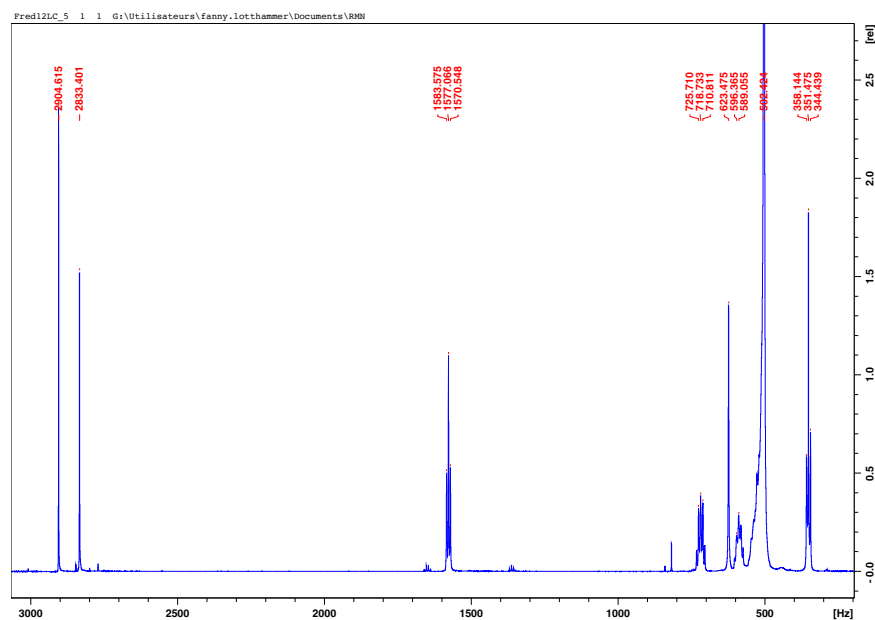
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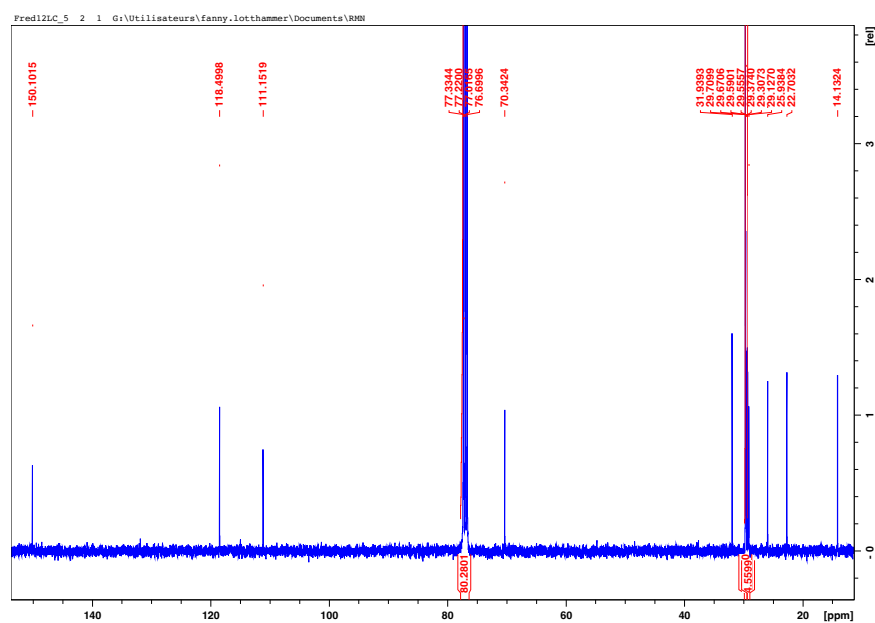
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(a)

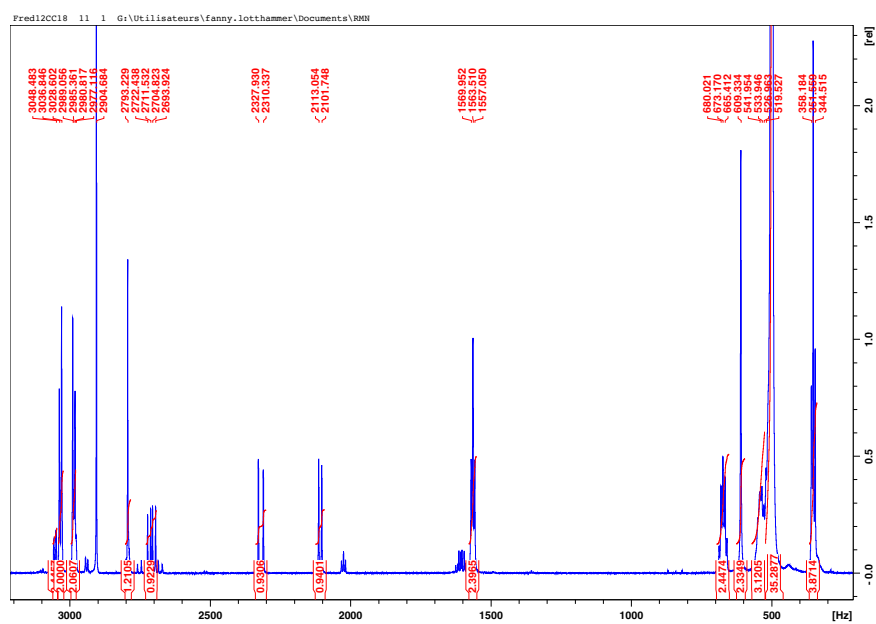


(b)

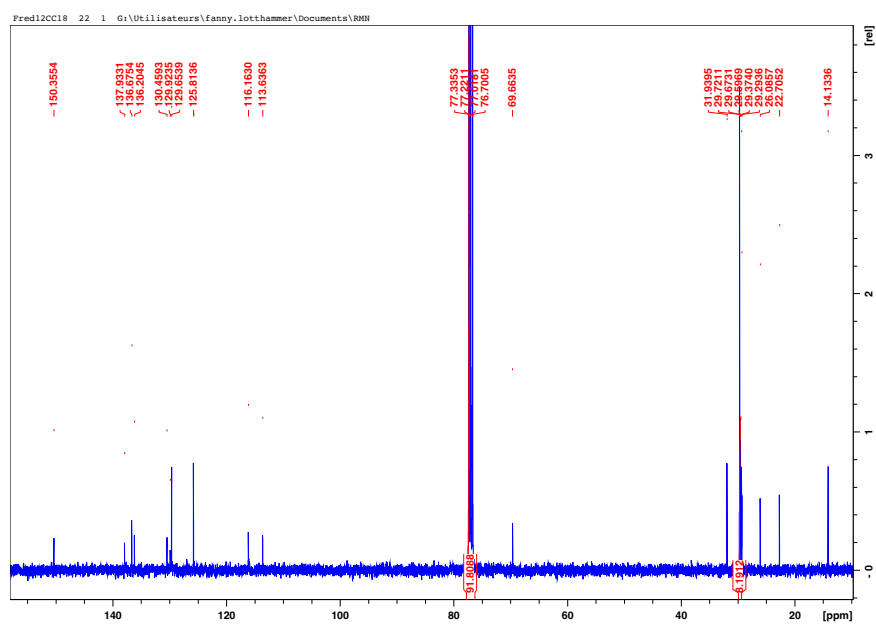


**Figure S1.** (a)  $^1\text{H}$  NMR and (b)  $^{13}\text{C}$  spectra of 1,4-dibromo-2,5-bis(octadecyloxy)benzene ( $\text{CDCl}_3$ ).

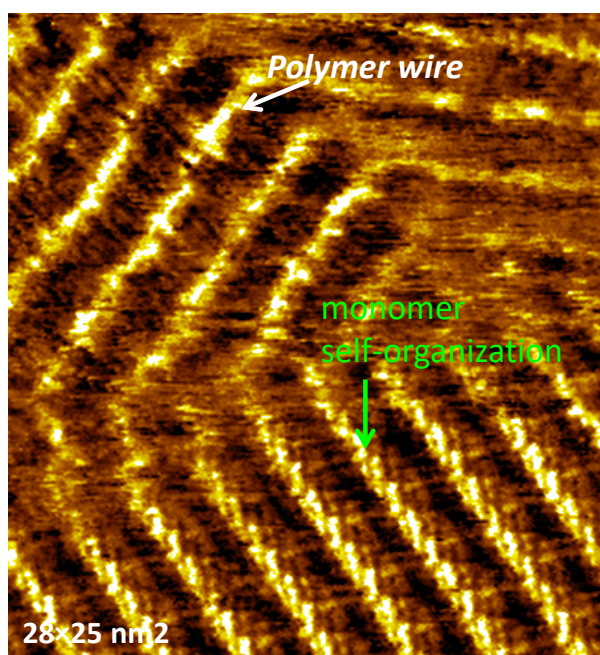
(a)



(b)

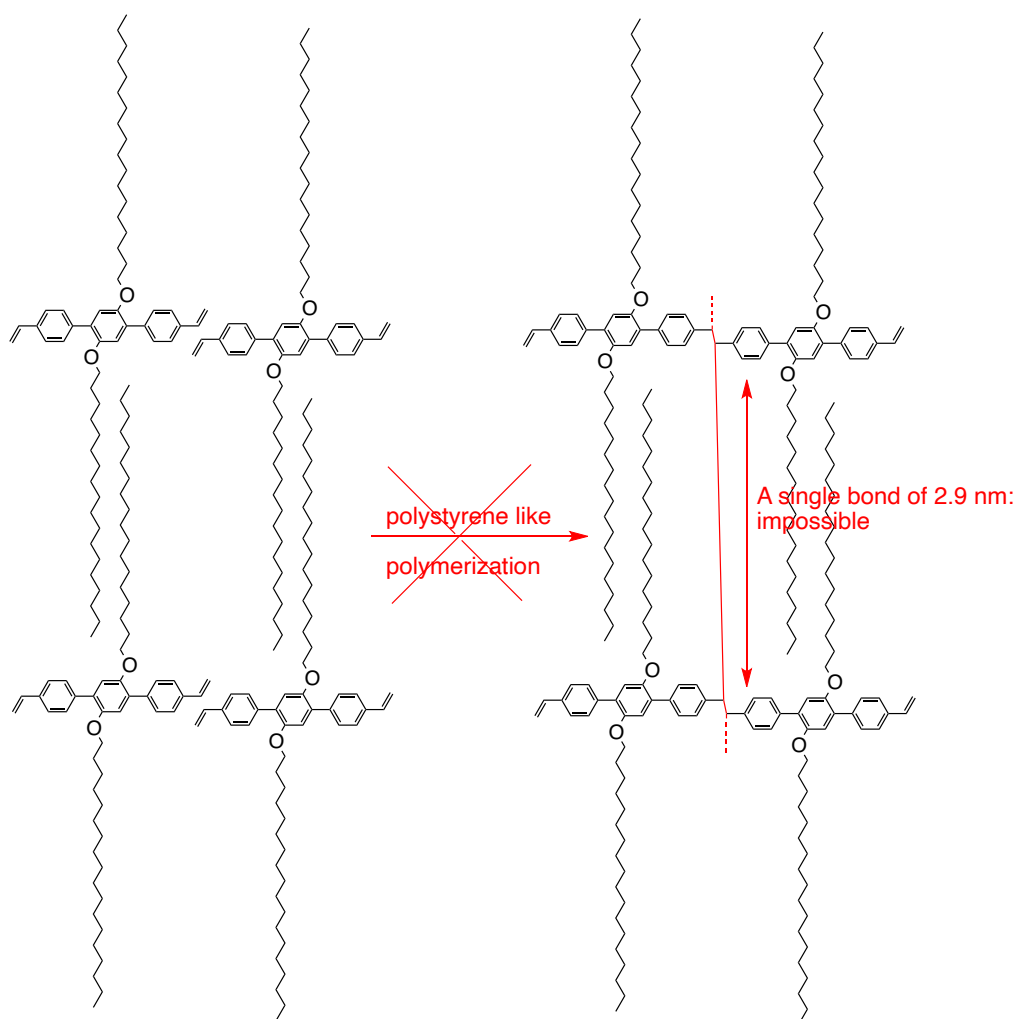


**Figure S2.** (a) <sup>1</sup>H NMR and (b) <sup>13</sup>C spectra of 1,4-bis(4'-vinylphenyl)-2,5-bis(octadecyloxy)benzene (CDCl<sub>3</sub>).

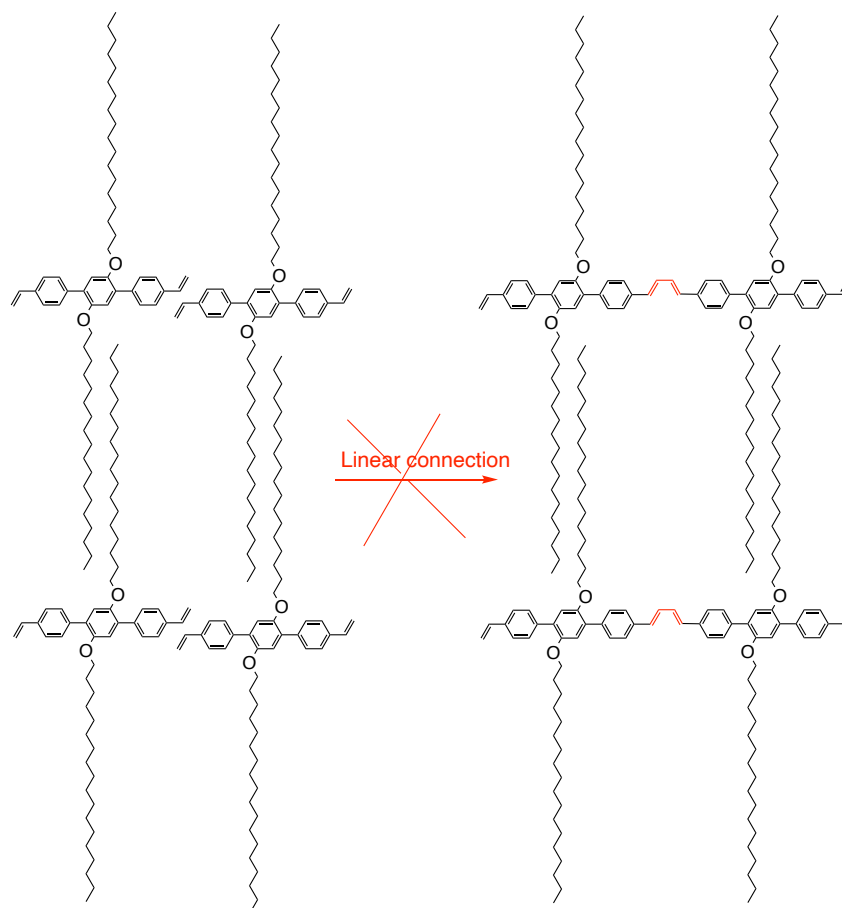


**Figure S3.** STM image ( $V_s = -0.5V$ ,  $I_t = pA$ ,  $28\text{ nm} \times 25\text{ nm}$ ) of vinyl-OC18 photo-polymerized (upper part) and unpolymerized (lower part) networks.

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**Figure S4.** Scheme of hypothetical polymerization of C=C bonds between adjacent vinyl-OC18 molecules as usually observed in the case of styryl-derivatives. The lateral alkyl chains are too long to allow the formation of C-C bond between molecules (highlighted in red).



**Figure S5.** Scheme of hypothetical polymerization of C=C bonds between consecutive vinyl-OC18 molecules (new bonds are highlighted in red). This type of reaction requires coinage metal surface, high temperature and UHV conditions.